Experimental Results Using Ammonia Plus Hydrogen in a S.I. Engine

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Abstract In the prospective to reduce greenhouse gas emission from vehicles, the use of hydrogen as fuel represents a possible solution. However, if proper engine running with hydrogen has been widely demonstrated, hydrogen storage onboard of the vehicle is a major problem. A promising solution is storing hydrogen in the form of ammonia that is liquid at roughly 9 bar at environmental temperature and therefore involves relatively small volumes and requires light and low-cost tanks. Moreover, liquid ammonia contains 1.7 times by volume as much hydrogen as liquid hydrogen itself. It is well known that ammonia can be burned directly in I.C. engines, however a combustion promoter is necessary to support combustion especially in the case of high-speed S.I. engines. As a matter of fact, the best (and carbon-free!) promoter is hydrogen, which has very high combustion velocity and wide flammability range, whereas ammonia combustion is characterised by low flame speed, low flame temperature, narrow flammability range (combustion is impossible if mixture is just slightly lean), high ignition energy and high self-ignition temperature.

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The experimental activity shown in the paper was aimed at determining proper air-ammonia-hydrogen mixture compositions for the actual operating conditions of a twin-cylinder 505 cm^3 S.I. engine. Hydrogen and ammonia are separately injected in the gaseous phase. The experimental results confirm that it is necessary to add hydrogen to air-ammonia mixture to improve ignition and to speed up combustion, with ratios that depend mainly on load and less on engine speed. This activity is correlated with a larger-scale project, founded by Tuscany Region, in which a partnership of research and industry entities has developed a fully-working plug-in hybrid electric vehicle equipped with a range-extending 15 kW IC engine fuelled with hydrogen and ammonia. Hydrogen is obtained from ammonia by means of on-board catalytic reforming.

Keywords Ammonia engine · Hydrogen engine · Alternative fuels · Carbon-free fuels · Ammonia reforming

Abbreviations

AIT	Auto ignition temperature
AMIE	Absolute minimum ignition energy
BTDC	Before top dead centre
CA	Crank angle
CNG	Compressed natural gas
COV	Coefficient of variation
DI	Direct injection
EBTE	Engine brake thermal efficiency
ECU	Electronic control unit
EC	Energy content (stoichiometric mixt)
EGR	Exhaust gas recirculation
FL	Flammability limits (gas in air)
HAER	Hydrogen-ammonia energy ratio
IC	Internal combustion
LFV	Laminar flame velocity
LHV	Lower heating value
IMEP	Inlet mean effective pressure
MBT	Maximum best torque
RPM	Revolution per minute
ON	Octane number
SCR	Selective catalytic reactor
SI	Spark ignition
ST	Stoichiometric
TDC	Top dead centre
UEGO	Universal exhaust gas oxygen
WOT	Wide open throttle
ρ	Density

1 Introduction

The main problem of electric vehicles is poor driving range due to low battery capacity. This drawback is enhanced by power requirement for lights and heating in winter.

Therefore in many cases range extenders are required, which use fuel to produce electricity when necessary [1–4]. Almost all present range extenders are based on conventional S.I. or C.I. engines, which are reliable and not expensive, but produce large green house gas emissions.

To produce carbon-free emissions, hydrogen can be employed as fuel in the range-extender engine (I.C. engine running ability with hydrogen has been widely demonstrated), but it reduces the range extending capacity, due to the scarce amount of hydrogen that can be stored on board. Moreover, as underlined by other authors [5], actually there is no existing infrastructure for hydrogen delivery and over 90 % of hydrogen production is still from reforming of fossil fuels such as natural gas, with the accompanying CO_2 emissions.

A solution to overcome this problem consists in storing hydrogen in the form of ammonia, which, at environmental temperature, is liquid at roughly 9 bar at environmental temperature and therefore involves relatively small volumes and requires light and low-cost tanks. Moreover, liquid ammonia contains 1.7 times by volume as much hydrogen as liquid hydrogen itself [6, 7].

Roughly 85 % of world ammonia production is based on steam reforming of natural gas using the well known Haber–Bosch process [8], but ammonia can be produced also electrochemically, or organically, or biologically, or by renewable sources: biomass energy, wind energy, solar energy, geothermal energy, hydroelectric energy can be used to electrolyse hydrogen from water and produce ammonia. These methods provide a number of scalable manufacturing routes that can be developed and employed in accordance with evolving market demand and economy.

The possibility to use ammonia as direct gasoline replacement has been concretely discussed since mid-1960s [9–12], even if previous attempts and a patent of 1938 attest the possibility of using a mixture of hydrogen, ammonia and nitrogen as fuel in internal combustion engines [13, 14]. Some experiences show that lone ammonia can be burned in IC engines. However, due to low flame temperature, low laminar burning velocity and high ignition energy, it is practical to use ammonia together with other fuels used as combustion catalysts. Some investigations attest [15–19] that the best one is hydrogen, showing that a small amount, added to air-ammonia mixture, is effective to speed combustion up.

The opposed and potentially complementary properties of hydrogen and ammonia give new prospective in engine combustion control. As aforesaid, ammonia is characterized by low flame speed (also with respect to gasoline) and narrow flammability range (combustion is impossible even with low excess air), high ignition energy and high auto-ignition temperature. On the other side,

Table 1 Combustion properties of ammonia, hydrogen and gasoline [21]

Properties	Ammonia	Hydrogen	Gasoline
LHV (MJ/kg)	18.8	120	44.5
FL (vol. %)	15–28	4.7–75	0.6–8
LFV (m/s)	0.015	3.51	0.58
AIT (°C)	651	571	230
AMIE (mJ)	8.0	0.018	0.14
ON (RON)	>130	>100	90–98
ρ (25 °C, 1 bar) (g/L)	0.703	0.082	740
ST (air/fuel) (mass)	6.04	34.3	~14.5
EC (st. mixt.) (MJ/kg)	2.8	3.3	2.7

hydrogen displays low ignition energy, high combustion velocity and wide flammability range that allows the engine to operate with very high air–fuel ratios.

A comparison of combustion properties of ammonia, hydrogen and gasoline are given in Table 1 [17–20].

Extensive analyses of ammonia production cost and of energy per unit of storage tank volume, in comparison with other conventional fuels (gasoline, compressed natural gas CNG, liquefied petroleum gas LPG, methanol, hydrogen) has been conducted by other authors [20]. The study shows that ammonia is the least expensive fuel in terms of cost per GJ stored onboard, while in terms of GJ/m^3 ammonia becomes the third, after gasoline and LPG. Moreover, ammonia is the cheapest fuel per 100 km driving range.

It is noteworthy resuming some data, shown in Table 2, related to a comparison of ammonia and hydrogen storage and driving range characteristics on a prototype vehicle based on a Ford Focus. Some of the original data were recalculated taking into consideration the Italian law that imposes 200 bars as maximum storage pressure on board. The power-train performance is characterized by 1.19 MJ/km shaft power and the efficiency of the ammonia engine has been taken the same as of the hydrogen engine. As it can be noted, the driving range of the NH_3 vehicle is much longer and hence less expensive (for ammonia it was assumed a cost of \$0.30/kg and for hydrogen an average cost of \$4/kg). Moreover, the tank of the ammonia car is about 6 times more compact.

Some additional advantages of ammonia in respect of hydrogen are commercial availability and viability, global distribution network, easy handling experience, etc., while the problem of its toxicity that can easily be overcome with the current control and storage technologies.

The experimental activity displayed in this paper was mainly aimed at developing a simple electronic hydrogen-ammonia injection system and determining appropriate air-ammonia-hydrogen mixture composition for each actual operating condition of a prototype engine and therefore at establishing the proper technical characteristics of the injection system.

This activity is correlated with a larger scale project, focused on a range-extended electric vehicle (briefly presented at the end of the paper) involving the

Table 2 Ammonia and hydrogen storage characteristics

Parameter	Unit	Ammonia	Hydrogen
Tank volume	Liter	60	200
Storage pressure	Bar	10	200
Energy on-board	MJ	814	393
Estimated driving range	km	340	165
Tank compactness	L/100 km	18	121

Table 3 Experimental engine specifications

Model	Lombardini LGW 523 MPI
Displacement	505 cm^3
Stroke	62 mm
Bore	72 mm
Compression ratio	10.7:1
Cooling system	Water cooled
Valves	2 per cylinder
Max power (gasoline)	21 kW @ 6,000 rpm
Max torque (gasoline)	39 Nm @ 2,200 rpm
Engine velocity at idle	1,100 rpm
Mass	49 kg

ammonia-plus-hydrogen I.C. engine and where the necessary flow of hydrogen comes from a special catalytic ammonia cracker (purposely realized within the project) that is heated by engine exhaust gases. No production of greenhouse gases occurs since ammonia does not contain carbon.

2 Engine Experimental Setup

The prototype engine derives from a 505 cm^3 Lombardini twin-cylinder S.I. engine, whose specifications are reported in Table 3. Hydrogen and ammonia are separately injected in the gaseous phase. Accordingly, the original intake manifold was modified to add electro-injectors for hydrogen and for ammonia to the original ones for gasoline. This is the only mechanical modification the original engine underwent.

As a whole, six electro-injectors are now located on the intake manifold (three for each duct). The injectors for ammonia and for hydrogen are conventional ones for CNG application with appropriate modifications to their inner parts.

Ammonia was stored in the liquid phase at room temperature and 9 bars. An heated vaporizer with a pressure regulator was placed before the electro-injectors. Careful attention was dedicated to the hydrogen-ammonia feeding line to avoid leakages and partial ammonia condensation before the injectors.

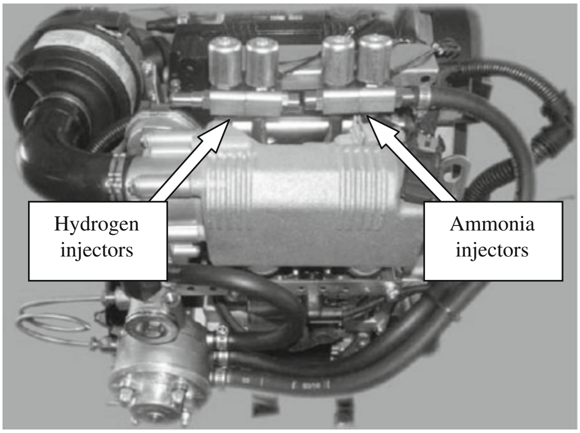


Fig. 1 The experimental engine with *ammonia* and *hydrogen injectors* in evidence

The original ECU was replaced with a fully-programmable one (MoTeC model M800) and set to drive the ignition system and the six electro-injectors for hydrogen, ammonia and gasoline (this last option, i.e. the use of gasoline, was kept in the prospective of a more flexible hybrid vehicle).

The engine was fully instrumented. A magnetic sensor was located on the camshaft for the correct phasing of the injection and ignition events. Thermal flow meters were adopted to measure hydrogen and ammonia consumption. Piezo-resistive pressure sensors gauged the intake and the exhaust pipes, while a special spark plug with integrated piezoelectric sensor gauged cylinder pressure. Pressure sensors were placed in the ammonia and in the hydrogen feeding lines. Thermocouples were located in the intake and exhaust pipes, as well as in the cooling and in the lubrication circuits. To measure fuel–air ratio (λ) a proportional O_2 (UEGO) sensor was placed in the exhaust pipe, while a chemiluminescence NO_x analyzer gauged the exhaust emissions. An optical encoder was placed on the frontal side of the crankshaft, while an AVL Indicom system performed data acquisition and processing. The intake air flow rate was controlled by the original motorized throttle valve.

Figure 1 shows a picture of the experimental engine with ammonia and hydrogen injectors in evidence.

3 Experimental Activity and Results

Preliminary tests were performed to verify the possibility to operate the engine with a mixture of air, ammonia and hydrogen and to determine proper injection timings and feeding line pressures of hydrogen and ammonia for suitable combustion at all speeds and loads. This first experimentation was performed mainly in view of producing hydrogen on board the vehicle by ammonia catalytic reforming, to verify whether the working temperature and the output limits in hydrogen flow

rate and pressure (roughly 1.35 Nm^3/h and 0.5 bar relative pressure) of the designed catalytic reformer were compatible with engine characteristics and needs.

This performance of the catalytic reformer was separately verified by experimental tests that proved full conversion of ammonia to hydrogen and nitrogen (whose flow rate to the engine is negligible compared to nitrogen flow rate due to air intake) at the designed temperature of 500 °C. Yet, ammonia conversion was proved to be almost complete even at as low reformer temperature as 450 °C, allowing security margin in case of exhaust gas temperature fluctuation. The thermal energy necessary for the catalytic reaction can be obtained from the exhaust gasses whose temperature, into the operative range examined, is always higher 550 °C. In addition, the reformer is electrically heated to overcome the problem of insufficient exhaust gas temperature during cold start transient.

Injection timings for hydrogen and ammonia were set at TDC of the passive cycle. Feeding line relative pressures for hydrogen was set at 0.4 bar, while for ammonia a relative pressure of 2.4 bar was utilised.

The next experimental activity was focused on determining the minimum hydrogen-to-ammonia energy ratios (HAER) that keep $COV_{imep} < 10$ %. This is considered the maximum value of cyclic variation for acceptable engine behaviour [22]. Tests were performed at various speeds (from 2,500 to 5,000 rpm with steps of 500 rpm) and loads (full and half load) with stoichiometric mixtures ($\lambda = 1$), taking the operating range of the engine connected to the electric generator into account. Forthcoming tests will explore engine behaviour with lean mixtures.

Ignition advance was set at MBT at every engine speed and load and for each experimental condition 100 cycles were recorded and analysed.

The experimentation evidenced two important issues, summarized as follows:

1. With the smallest acceptable HAER, 40° to 42° BTDC ignition timing gives the best results at every engine speed and load. This spark advance is 10° to 15° larger than with gasoline and can be addressed to high ignition energy and low flame speed that characterize and protract ammonia combustion, leading to larger heat loss through cylinder walls and less residual expansion than with gasoline, with consequent less thermal efficiency.
2. Engine COV_{imep} rapidly increases as HAER falls below a certain value, as Fig. 2 proves for full load and $\lambda = 1$ at 3,000 and 4,000 rpm. In this case COV_{imep} sharp increase occurs below a HAER value of roughly 6–7 %, yet engine behaviour remains acceptable up to a HEAR value of roughly 5 %.

Conservatively, the HAER below which engine COV_{imep} rapidly increases have been considered as the “practical” minimum HAER that is given in Fig. 3 versus engine speed with $\lambda = 1$, at full and half load.

Figure 4 displays brake power vs. engine speed at WOT and $\lambda = 1$ with gasoline and with ammonia plus the above-mentioned minimal sufficient amounts of hydrogen, proving that in the second case power is roughly 10 % less at low rpm and 25 % less at high rpm. This is due to mixture poor volumetric heating value, because of the high specific volume of ammonia and hydrogen, and to ammonia low flame speed that penalizes the more, the faster the engine runs.

Fig. 2 COV_{imep} versus HEAR at 3,000 and 4,000 rpm, WOT, $\lambda = 1$

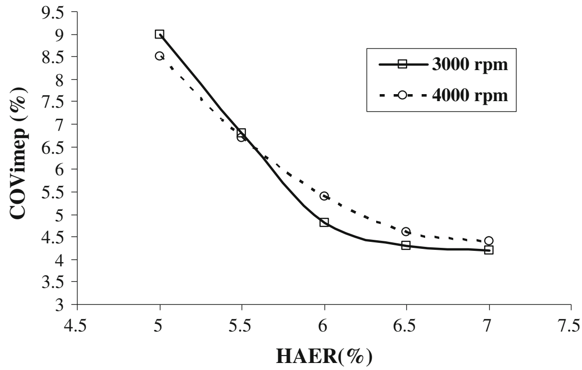


Fig. 3 Minimum HEAR versus engine speed at full and half load, $\lambda = 1$

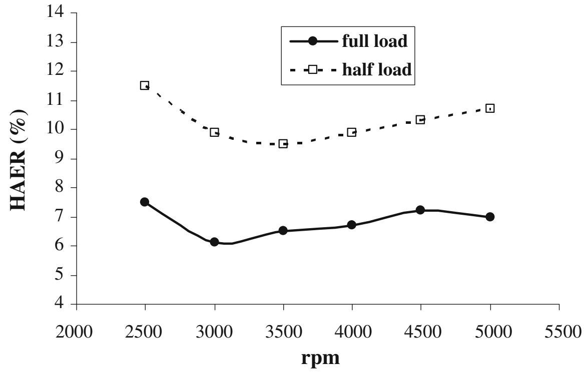
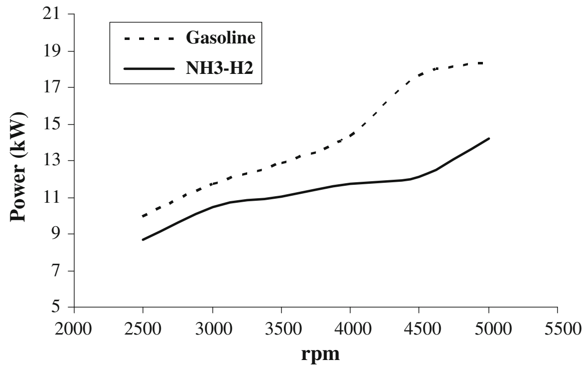


Fig. 4 Brake power versus engine speed with gasoline and with ammonia plus hydrogen at WOT, $\lambda = 1$



NO_x is the only meaningful pollutant found in the exhaust emissions (unburned hydrocarbons from lubricant are negligible and the presence of ammonia in the exhaust gas was not measured). Figure 5 displays NO_x emission vs. engine speed with the minimum HAER at full and half load, keeping $\lambda = 1$. At full load, NO_x maximum emission is 1,700 ppm at 3,000 rpm. Due to the lower combustion temperatures, NO_x emission is always lower at half load, with a maximum of

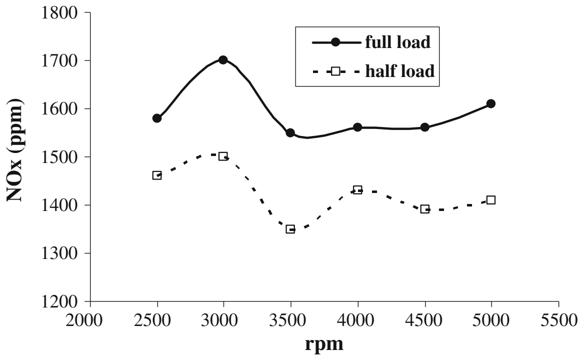


Fig. 5 NO_x versus engine speed with ammonia plus hydrogen at full and half load, $\lambda = 1$

1,500 ppm, still located at about 3,000 rpm. Yet, NO_x emission is not a problem, since, in the case of stoichiometric mixture, NO_x can be effectively abated by a normal reducing catalyst and, in the case of lean mixture, the use of a SCR is eased by the presence of ammonia onboard.

3.1 Cold Start Procedure

Hydrogen-to-ammonia ratio must be considerably increased to guarantee correct engine cold start, as data on Table 4 prove. Cold start feeding conditions must be kept for few seconds after starting, with the engine at idle (1,800 rpm, quite high idle speed in respect of around 1,100 rpm with gasoline). Then hydrogen-to-ammonia ratio is progressively reduced and engine speed increased to reach the required operating conditions.

Since hydrogen flow rate is higher than the one provided by the catalytic reformer, a suitable amount of hydrogen must be stored in a tank that will be recharged during engine normal running. Solutions are being studied to reduce the cold-start requirement of hydrogen flow rate to the level provided by the catalytic reformer. Among them, high engine compression ratio (allowed by very high ammonia octane number) and special solutions for ignition are worth mentioning.

4 The Range-Extended Electric Vehicle

The ammonia-hydrogen engine was installed on prototype range-extended electric vehicle that derives from Effedi Gasolone 35, a small commercial vehicle conceived for garbage collection, originally equipped with a Diesel engine.

This vehicle displays two important features:

1. It has a flexible chassis that is suitable for the transformation to hybrid (several new devices must be installed on board, such as all the electric and electronic devices, the hydrogen generator, the ammonia tank, etc.);

Table 4 Cold start feeding conditions

H_2 flow rate	2.6 Nm^3/h
H_2 feeding line relative pressure	0.4 bar
NH_3 flow rate	0.54 Nm^3/h
NH_3 feeding line relative pressure	2.1 bar
HAER	360 %

Fig. 6 Final assembly of the vehicle, ready for road test

2. It is a typical example of vehicle for city use; as a matter of fact it is the smallest available one with 3.5 t capacity and it is characterized by high manageability.

Range-extended electric vehicles for garbage collection are especially suited for city centres where noise and pollution are very important issues and where these vehicles can work in pure electrical mode (sometimes garbage is collected during the night), restricting the use of the I.C. engine to the transfer travels.

The prototype is a series hybrid: the vehicle is driven by the electric motor with no mechanical connection to the I.C. engine that only runs a generator to recharge the batteries.

All the components of the power train, i.e. the I.C. engine, the generator, the electric motor, the electronic controls and devices, etc. were expressly studied, designed and realised.

Because of the toxicity of gaseous ammonia, a suitable monitoring system was integrated into the vehicle. It is based on a modular architecture, which allows the integration of several sensors in a scalable plug-an-play structure and provides data pre-elaboration.

Three ammonia sensors are located in different places of the vehicle: one is placed inside the cockpit, for the safety of the driver; another sensor is placed near both the ammonia tank and the catalytic reactor, to monitor possible ammonia leakages, and the last one is at the exit of the tailpipe to detect the presence of unburned ammonia. The system alarms were settled on a threshold of 20 ppm of ammonia for inside the vehicle and of 100 ppm for outside.

The final assembly of the vehicle, ready for road test, is showed on Fig. 6.

5 Conclusions

Ammonia represents a hydrogen carrier and can be effectively utilized as fuel in IC engines, provided that a small percentage of other fuels is added as combustion catalyst. Among them, the best one is hydrogen, which can be obtained directly from ammonia on board the vehicle by means of a catalytic reformer.

In this experimental activity a simple electronic fuel injection system, that injects ammonia and hydrogen in the gaseous phase, was designed and implemented on a 505 cm^3 twin-cylinder S.I. engine that was mechanically modified only as concerns the intake manifold, to host the electro-injectors for ammonia and hydrogen.

The final aim of the study is the design and construction of an electric vehicle, where the ammonia-plus-hydrogen engine is employed as range extender and hydrogen is obtained from ammonia by on-board catalytic reforming.

The experimental results confirm the need to speed combustion up by adding hydrogen to air-ammonia mixture, with ratios that mainly depend on load. The minimum HAER to get correct engine behaviour (i.e. $COV_{imep} < 10\ \%$) is roughly 6–7 % at full load and 10–11 % at half load.

Keeping $\lambda = 1$ on the whole, engine stability increases increasing the HAER, as expected.

NO_x is the only meaningful pollutant found in the exhaust emissions (unburned hydrocarbons from lubricant are negligible), with a maximum of 1,700 ppm at full load and 3,000 rpm.

The presence of ammonia in the exhaust gas was not measured at test bench. However, an ammonia sensor is placed at the exit of the exhaust pipe on the vehicle for the next road testing activity.

No meaningful mechanical inconvenience occurred during the described experimental activity. Nevertheless, long-time reliability of the injection system for ammonia and for hydrogen has to be verified.

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